Applied Surface Science 288 (2014) 416–422

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Influence of accelerating gas flow rate on the particle cohesion in room temperature cold sprayed scattering layer for plastic-based dye-sensitized solar cells

Xue-Long He, Guan-Jun Yang*, Chang-Jiu Li*, Cheng-Xin Li

State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, PR China

ARTICLE INFO

Article history:
Received 7 July 2013
Received in revised form 29 August 2013
Accepted 9 October 2013
Available online 18 October 2013

Keywords:
Dye-sensitized solar cells
Room temperature cold spray
Microstructure
Cohesion
Reflectance
Scattering layer

ABSTRACT

Mesoporous TiO_2 coating was prepared by room temperature cold spraying with submicro-sized anatase TiO_2 powder for scattering layer in plastic-based DSCs. The effect of accelerating gas flow rate on the microstructure, cohesion and optical property of the as-prepared TiO_2 scattering layers was investigated. Results showed that the cohesion of the TiO_2 scattering layer increased with the increase of accelerating gas flow rate due to the improved particle–particle connection by the particle impact at an increased velocity. The light-reflecting ability of the TiO_2 scattering layers increased with the increase of coating thickness from 2 to 10 μm and decreased with the increase of accelerating gas flow rate from 3.5 to 7.5 L/min. By adding the scattering layer to the photoanode of the plastic-based DSCs, the conversion efficiency of the plastic-based DSCs was increased by a factor of 21% to 4.70%.

1. Introduction

Plastic-based dye-sensitized solar cells (DSCs) are being rapidly developed, owing to their advantages such as low cost, lightweight, flexibility, environmental friendliness and possibly colorful decorative appearance [1]. However, the cell efficiency is limited by the insufficient electron transport property of the nano-porous TiO_2 film in which only a weak connection is formed during the preparation of TiO_2 film at low temperature [2,3]. A feasible approach to improve the conversion efficiency is to add a scattering layer composed of large particles with a diameter of 100–400 nm on the surface of TiO_2 nanocrystalline (NC) layer [4–6]. Typically, TiO_2 scattering layer was prepared by casting TiO_2 paste with an organic binder on glass substrate, followed by sintering at a temperature above 450 °C to burn off the organic binder. However, for the plastic substrate-based DSCs, this conventional preparation method using high-temperature annealing is not applicable, owing to the low heat-resistance temperature (150 °C) of the plastic substrates [7]. Therefore, it is still a challenge to effectively prepare light scattering layer for plastic-based DSCs.

Room temperature cold spraying (RTCS, also called vacuum cold spray) method can be used to deposit nano-TiO_2 coating with good particle–particle connection on plastic substrate for photoanode of flexible DSCs [8,9]. During the RTCS process, TiO_2 powder particles are accelerated to a high velocity (100–300 m/s) by a gas flow and deposited on a substrate surface to form TiO_2 coating in a low pressure environment of several hundreds of pascals. The impact of powder particles at a high velocity on the substrate surface generates a high pressure pulse, leading to the formation of good connection between TiO_2 particles [8,10]. Owing to the feature of low-temperature process, RTCS process may be used to solve the problem involved in the deposition of scattering layer with good particle–particle connection in plastic-based DSCs.

In this study, RTCS method was used to prepare TiO_2 coating as light scattering layer using submicro-sized anatase TiO_2 powder. The ultrasonic test was used to quantitatively evaluate the cohesion of the coatings. The influence of accelerating gas flow rate on microstructure, cohesion and optical property of the coatings was explored to aim at understanding the microstructure/property relationship. The performance of these coatings as scattering layers for the plastic DSCs was investigated.

2. Experimental

2.1. TiO_2 coating preparation

Commercially available submicro-TiO_2 (anatase) powder (Fig. 1) of 100–200 nm in diameter was used as feedstock in this study for

* Corresponding authors. Tel.: +86 29 82665299; fax: +86 29 82660970.
E-mail addresses: ygj@mail.xjtu.edu.cn (G.-J. Yang), licj@mail.xjtu.edu.cn (C.-J. Li).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.10.049

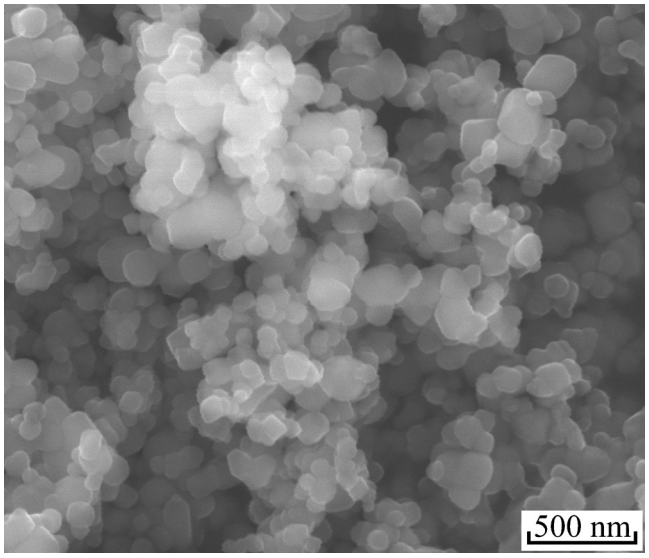

Fig. 1. Surface morphology of the submicro-TiO_2 powder.

light scattering layer. TiO_2 coatings were deposited by a home-developed RTCS system. The RTCS system consists of a vacuum pump, a vacuum chamber, a power feeder, an accelerating gas feeding unit, a particle accelerating nozzle, a two dimension worktable and a control unit [11,12]. Helium was used as the accelerating gas at a pressure of 0.2 MPa. The chamber pressure during spraying was about 10^2–10^3 Pa. The standoff distance from the nozzle exit to the substrate surface was 10 mm. The relative traverse speed of the nozzle over the substrate was 20 mm/s.

To assemble the plastic-based DSC, the TiO_2 NC layer was deposited with the P25 nano-TiO_2 powder (Degussa, 70% anatase and 30% rutile) with a diameter of 25 nm at a gas flow rate of 7 L/min on indium-doped tin oxide coated polyethylene naphthalate (ITO-PEN, PECF-IP, 15 $\Omega\,sq^{-1}$, Peccell) substrate. For the deposition of TiO_2 scattering layer, the submicro-TiO_2 powder with a diameter of 100–200 nm was used, and the accelerating gas flow rate was set at 3.5, 4.5, 6, and 7.5 L/min.

2.2. Characterization of TiO_2 coatings

The microstructure of TiO_2 scattering layer was examined by a field emission scanning electron microscope (FESEM, QUANTA 600F). The light-reflecting ability of the TiO_2 scattering layer was evaluated by measuring the reflectance spectrum of the TiO_2 scattering layer by a UV–vis spectrophotometer equipped with an integrating sphere setup (JASCO V-570). The sphere as well as the reference plates is coated with $BaSO_4$. Considering the flexibility of the ITO-PEN plastic substrate, the TiO_2 scattering layers were deposited on a rigid conductive FTO-glass substrate (TEC 15, LOF) to facilitate the measurement. In all measurements, the light was incident from the bare FTO-glass side to the coated side. The coating thickness was measured by a profilometer (XP-2, AMBIOS Technology, Inc., USA).

The cohesion of the TiO_2 scattering layer was evaluated by ultrasonic test using an ultrasonic cleaner (VGT-1730T, 120 W, Xi'an Coming Ultrasonic Equipment Instrument Co., Ltd. China). To facilitate the measurement, the TiO_2 scattering layers were deposited on FTO-glass substrate. Before coating deposition, the FTO-glass substrates were weighed on an electronic analytical balance (BT224S, Sartorius, Germany) with a precision of 0.1 mg. After the scattering layer deposition, the TiO_2 scattering layers were ultrasonic tested in ethanol solution for different durations. Then the scattering layers were dried at 100 °C for 10 min to obtain the dry weight. The relative weight loss was used to evaluate the cohesion of the TiO_2 scattering layer, as the thickness of all samples was kept at 10 μm. The cross-sectional morphologies of the scattering layers after different ultrasonic test durations were also observed by FESEM.

2.3. Fabrication and characterization of plastic-based DSCs

To prepare the photoanode for the plastic-based DSCs, the TiO_2 NC layer with a TiO_2 scattering layer on the ITO-coated plastic substrate was immersed in an absolute ethanol solution of 0.3 mM N719 dye (Solaronix) for 24 h, followed by cleaning with absolute ethanol. Then, the photoanode was assembled with plastic Pt CE using a 60 μm thick Surlyn film (1702, DuPont) as a spacer. The electrolyte solution was introduced into the cell through a hole pre-drilled on the back of the plastic CE, and then the hole was sealed up using a UV resin (ThreeBond). The electrolyte solution was composed of 0.6 M DMPII (Institute of Plasma Physics), 0.05 M I_2 (Aldrich), 0.1 M LiI (Aldrich), and 0.5 M 4-*tert*-butylpyridine (Acros) in dehydrated acetonitrile (Aldrich).

The photovoltaic performance of the plastic-based DSCs was measured using a solar simulator (100 mW cm^{-2}, Oriel 94023A, Newport) equipped with a Keithley 2400 digital source meter. The active area of the photoanode was 0.4 cm^2. The monochromatic incident photon-to-current conversion efficiency (IPCE) of the DSCs was measured by an IPCE measurement system (7-SCSpec, Beijing 7-star Optical Instruments Co. Ltd).

3. Results and discussion

3.1. Microstructure of the TiO_2 scattering layer

Fig. 2 shows the surface morphologies of the TiO_2 scattering layers prepared by RTCS method under different accelerating gas flow rates. As can be seen from Fig. 2, the surface morphologies of the TiO_2 scattering layers prepared under different accelerating gas flow rates were similar. The scattering layers were formed by the stacking of TiO_2 particles with a size of 100–200 nm which was comparable to that in spray powder (Fig. 1). It is known that the impact of solid particles on the substrate surface forms a coating during the RTCS process [13]. In order to investigate whether the TiO_2 primary particles fractured during the high velocity impact in the RTCS process, the cross-sectional morphologies of the fracture TiO_2 scattering layers were observed. Fig. 3 shows the cross-sectional morphologies of the fracture TiO_2 scattering layers prepared under different accelerating gas flow rates. It was obvious that the TiO_2 particles in all the scattering layers presented a similar nearly spherical morphology comparable to the spray powder particles (Fig. 1). This result suggested that the powder particle did not fracture or deform significantly during the coating deposition.

3.2. Cohesion of the TiO_2 scattering layer

The good particle–particle connection in the scattering layer is essential for the application of scattering layer. In this study, in order to estimate the cohesion of the TiO_2 scattering layer, an ultrasonic test was used. Fig. 4 shows the relative weight loss of the TiO_2 scattering layer prepared under different accelerating gas flow rates as a function of ultrasonic test duration. As can be seen from Fig. 4, the change of the relative weight loss of the TiO_2 scattering layer prepared under different accelerating gas flow rates exhibited the similar dependency with the ultrasonic test duration. The relative weight loss of the scattering layer increased with the increase of ultrasonic test duration. However, the specific weight loss was significantly different. After 120 s ultrasonic test, the relative weight loss of the scattering layer decreased from 80 to 11%